Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

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Available online: 20 Mar 2012

To cite this article: Guan-Yeow Yeap, Arwa Alshargabi, Masato M. Ito, Wan Ahmad Kamil Mahmood & Daisuke Takeuchi (2012): Synthesis and Anisotropic Properties of Azo-Bridged Benzothiazole-Phenyl Esters, Molecular Crystals and Liquid Crystals, 557:1, 126-133

To link to this article: http://dx.doi.org/10.1080/15421406.2011.637744

*Mol. Cryst. Liq. Cryst.*, Vol. 557: pp. 126–133, 2012

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2011.637744



# Synthesis and Anisotropic Properties of Azo-Bridged Benzothiazole-Phenyl Esters

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*A new series of benzothiazole-phenyl esters intersected by azo N=N has been isolated and their structures were characterized. These compounds exhibit enantiotropic nematic phase. The transition temperatures and the enthalpy values associated with these derivatives were found to be dictated by the variation of the lengths of the flexible alkoxyl chains ($OOCC_nH_{2n+1}$ where n adopts even numbers from 5 to 17). A noteworthy characteristic of this series is the clearing temperatures, which decrease upon lengthening of the alkoxyl chains from* n = *5 to* n = *17. A descending stability associated with the nematic phase range was also observed when the carbon number in the alkyl group increased. A comparative study between the title compounds and 6-ethoxy-2-(4-alkanoxybenzylidenamino)benzothiazole shows that the present compounds favor the formation of N phase while the previously reported analogs, which contain C=N instead of N=N, exhibited enantiotropic N and SmC phases.*

**Keywords** Azo linkage; benzothiazoles; enantiotropy; nematic phase; phenyl esters

## 1. Introduction

Heterocyclic units are important for thermotropic liquid crystals owing to their ability to impart lateral and/or longitudinal dipoles combined with changes in the molecular shape [1–3]. Furthermore, the incorporation of heteroatoms results in considerable changes in the corresponding liquid crystalline phases and/or in the physical properties of the observed phases as most of the heteroatoms (N, O, and S) commonly introduced are more polarizable than carbon [4]. As such, these heteroatoms are capable to influence the formation of mesomorphic phases [5]. The heterocyclic units, which have been widely used as cores in liquid crystals include pyridine [6], thiophene [7], and 1,3,4-thiadiazole [8]. Recently, benzothiazole derivatives have also been found to exhibit mesomorphic properties [9, 10].

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The study on these benzothiazole derivatives has actually been driven by the understanding that these materials possess electrical properties as shown by other calamitic compounds [11, 12]. This can be exemplified by the fast hole transport property of calamitic liquid crystal 2-(4-heptyloxyphenyl)-6-dodecylthiobenzothiazole as reported by Funahashi and Hanna [13, 14]. This finding has helped to conclude that the liquid crystalline compounds incorporating a benzothiazole-fused ring exhibit good hole transporting properties with a low ionization potential making them of potential interest as hole transporting materials in organic light-emitting devices (OLEDs) [13–15]. Several years later, Prajapati and Bonde had again reported two mesogenic homologous series which comprised of 6-substituted-benzothiazoles, but they used the azo (N=N) as linking group [16].

In this report, we describe the synthesis and mesomorphic properties of a homologous series of 4-((6-ethoxybenzothiazol-2-yl)diazenyl)phenylalkanoate (nEBTHDZ) in which the benzothiazole is connected to an aromatic ester by crossing through an azo (N=N) linkage. The length of the alkoxyl group $OOCC_nH_{2n+1}$ varies in even parity wherein $n$ ranges from 5 to 17. A comparative study with the analog having the C=N linkage is also documented in this report.



## 2. Expermintal

### *2.1 Reagents*

4-Dimethylaminopyridine (DMAP) was obtained from Merck (Germany). Sodium nitrite and phenol were purchased from M&R and Sigma-Aldrich, respectively. 2-amino-6-ethoxybenzothiazole, fatty acids ($C_nH_{2n+1}COOH$ where $n$ = 11, 13, 15, and 17) and acid chloride for fatty acid ($C_nH_{2n+1}COCl$ where $n$ = 5, 7 and 9), and N,N′-dicyclohexylcarbodiimide (DCC) were obtained from Acros Organics (USA). All solvents and reagents were used without further purification.

### *2.2 Characterization*

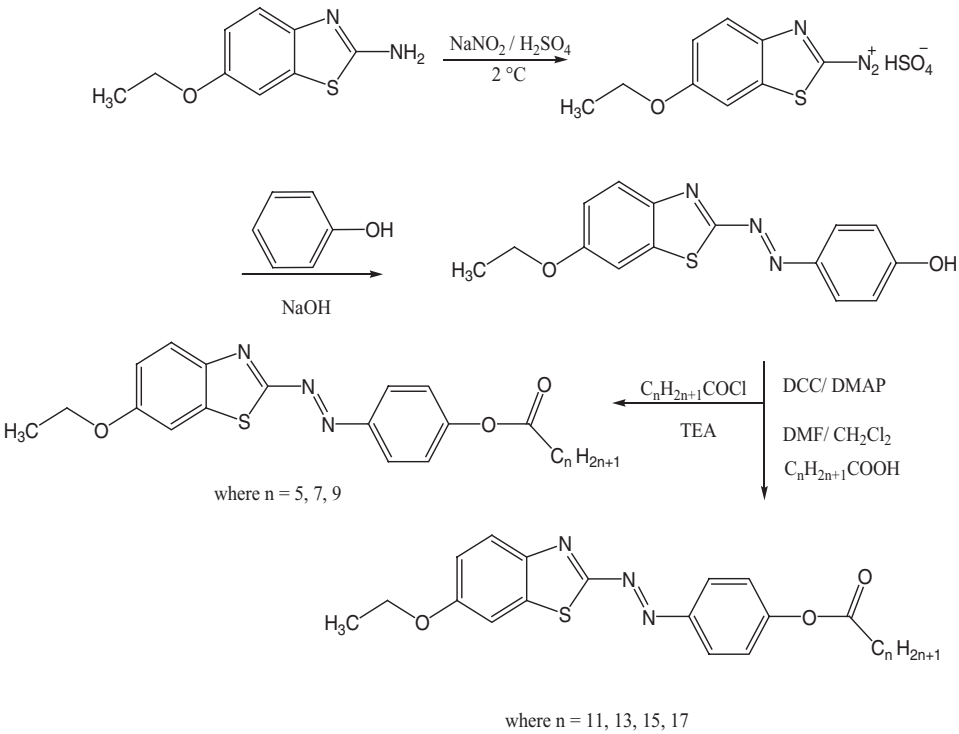
Infrared spectra for all intermediates and title compounds were obtained from Perkin Elmer 2000 FT-IR spectrophotometer in which the samples were mixed with KBr. The spectra were recorded in the range of 4000–400 $cm^{-1}$. CHN microanalyses were carried out on Perkin Elmer 2400 LS Series CHNS/O analyzer. $^1$H-NMR as well as $^{13}$C-NMR spectra were recorded in $CDCl_3$ and DMSO-$d_6$ using Bruker 300 MHz and 500 MHz UltrashieldTM FT-NMR spectrometers. Tetramethylsilane (TMS) was used as internal standard.

The phase-transition temperature and associated enthalpy values were determined by using a differential scanning calorimeter Seiko DSC6200R operated at a scanning rate of $\pm 5^{\circ}C\ min^{-1}$ both on heating and cooling. Texture observation of the mesophase was carried out by using Carl Zeiss Axioskop 40 polarizing microscope equipped with a Linkam LTS350 hot stage and TMS94 temperature controller. Phase identification was performed by comparing the observed textures with those reported in the literature [17, 18].

The synthetic route toward the formation of 4-((6-ethoxybenzothiazol-2-yl)azenyl)-phenylalkanoate (**nEBTHDZ**) is illustrated in Scheme 1.

### *2.3 Synthesis*

*2.3.1 Synthesis of 4-((6-ethoxybenzothiazol-2-yl)azenyl)phenol,* ***EBTHDZ-OH****.* A solution of 20 ml dilute sulphuric acid (60%) was added to 6-methoxy-2-aminobenzothiazole




**Scheme 1.** Synthetic scheme of 4-((6-ethoxybenzothiazol-2-yl)azenyl)-phenylalkanoate ***n*EBTHDZ**.

(1 g, 5.1 mmol) which was dissolved in glacial acetic acid, and the resulting mixture was cooled to 0°C. Sodium nitrite (0.35 g, 5.1 mmol) in 12.5 ml water was then added dropwise to the cold mixture and stirred for 1h in the ice bath. Phenol (0.47 g, 5.1 mmol), which was earlier dissolved in 15 ml ethanol, was cooled to 0°C and the diazonium salt solution was added dropwise at the temperature below 5°C. The mixture thus obtained was stirred for 1 h. The pH was increased to 6–7 by the addition of 1N NaOH, and the mixture was subsequently stirred for 1h in the ice bath. Finally, water was added to the resulting mixture and the precipitate was collected by filtration. The product was recrystallized from ethanol. Yield: 1 g (70.4%) and m.p. 286°C–287°C. IR (KBr) $\nu_{max}/cm^{-1}$: 3300–2600 (OH broad), 3042 (C−H aromatic), 1605, 1579 (C=C aromatic, C=N thiazole), 2943 (C−H aliphatic), 1057 (bezothiazole), 1135 (C-O). $^1$H-NMR (500MHz, DMSO-$d_6$) $\delta$/ppm: 8.0 (s, 1H, ArH), 7.8 (J = 6 Hz, d, 2H, Ar), 7.6 (d, 1H, ArH), 7.1 (J = 6.9 Hz, d, 1H, ArH), 7.01 (J = 6.9 Hz, d, 2H, ArH), 4.1 (J = 7.2 Hz, q, 2H, $-OCH_2$), 1.39 (J = 6.6 Hz, t, 3H, $-CH_3$).

*2.3.2 Synthesis of 4-((6-ethoxybenzothiazol-2-yl)azenyl)phenylalkanoate,* ***nEBTHDZ****, where n = 5,7, and 9.* The phenol **EBTHDZ-OH** (0.5 g, 1.67 mmol) was dissolved in 20 ml THF, and the flask containing this phenolic solution was placed in an ice bath. 1.67 mmol acid chloride $C_nH_{2n+1}COCl$ (where $n$ = 5, 7, and 9) in 20 ml THF was then added dropwise to this solution with stirring for 1 h. The 0.5 ml of triethylamine was then added dropwise to the resulting mixture. The solution was allowed to reach room temperature after stirring in the ice bath for 1 h and then stirred for another 12 h. The solid thus formed was filtered out and the solvent was evaporated. The precipitate was collected and recrystallized three times from ethanol to yield orange crystals.

The analytical data for the representative compound **9EBTHDZ** are summarized as follows:

*4-((6-ethoxybenzothiazol-2-yl)azenyl)phenyldecanoate,* ***9EBTHDZ***: IR (KBr) $\nu_{max}/cm^{-1}$: 3087 (C−H aromatic), 2927, 2859 (C−H aliphatic), 1758 (C=O ester), 1601 (C=C aromatic) 1590 (C=N thiazole). $^1$H-NMR (300 MHz, $CDCl_3$) $\delta$/ppm: 0.88 (J = 6.9 Hz, t, 3H, $CH_3$−), 1.2–1.4 (m, 12H, −$(CH_2)_6$−),1.5 (J = 6.9 Hz, t, 3H, $CH_3$−$CH_2$−O−), 1.7 (quint, J = 6.9 Hz, 2H, −$\underline{CH_2}$−$CH_2$−COO), 2.5 (J = 7.5 Hz, t, 2H, −$\underline{CH_2}$−COO−), 4.1 (J = 6.9 Hz, q, 2H, $CH_3$−$\underline{CH_2}$−O−), 7.1 (J = 9 Hz, d, 1H, Ar−H), 7.2 (J = 8.4 Hz, d, 2H, Ar−H), 7.3 (s, 1H, Ar−H), 8.0 (J = 8.1 Hz, d, 1H, Ar−H), 8.09 (J = 9 Hz, d, 2H, Ar−H). $^{13}$C-NMR (500 MHz, $CDCl_3$) $\delta$/ppm: 173.19 (COO), 171.77 (C=N), 159.11, 154.43, 149.28, 147.38, 136.38, 125.88, 125.37, 122.60, 116.98, 104.91 for aromatic carbons, 64.21 (−O−$CH_2$−$CH_3$), 34.45, 31.93, 29.69, 29.66, 29.61, 29.46, 29.36, 29.26, 29.10, 24.87, 22.70 for methylene carbons [$CH_3$−$(CH_2)_8$−COO−], 14.77 (−O−$CH_2$−$CH_3$), 14.14 [$CH_3$− $(CH_2)_8$−COO−].

*2.3.3 Synthesis of 4-((6-ethoxybenzothiazol-2-yl)azenyl)phenylalkanoate* ***nEBTHDZ****, where n = 11, 13, 15, and 17.* Appropriate fatty acid $C_nH_{2n+1}COOH$ in which $n = 11$, 13, 15, and 17 (1.67 mmol) was dissolved in 5 ml DMF and the solution was then added to compound **HO-EBTHDZ** (0.5 g, 1.67 mmol) which was dissolved in the same solvent. N,N′-dimethylaminopyridine (DMAP) (0.195 g, 1.67 mmol) and 1,3-dicyclohexylcarbodiimide (DCC) (0.329 g, 1.67 mmol) dissolved in 15 ml $CH_2Cl_2$ were then added to this solution. The resulting mixture was stirred at room temperature for 12 h. The mixture was then filtered. The water was added and then the product was extracted by dichloromethane. The organic phase was washed with water, dried over sodium sulphate anhydrous, and the solvent was removed by slow evaporation. The orange solid thus formed was recrystallized from ethanol.

The analytical data for a representative compound **13EBTHDZ** is described as follows:

*4-((6-ethoxybenzothiazol-2-yl)azenyl)phenyltetradecanoate,* ***13EBTHDZ****:* IR (KBr) $\nu_{max}/cm^{-1}$: 3042 (C−H aromatic), 2922, 2850 (C−H aliphatic), 1757 (C=O ester), 1601 (C=C aromatic) 1590 (C = N thiazole). $^1$H-NMR (300 MHz, $CDCl_3$) $\delta$/ppm: 0.8 (t, J = 6.6 Hz, 3H, $CH_3$−), 1.2–1.4 (m, 20H, −$(CH_2)_{10}$−),1.4 (J = 6.9 Hz, t, 3H, $\underline{CH_3}$−$CH_2$−O−), 1.7 (J = 6 Hz, quint, J = 2H,−$\underline{CH_2}$−$CH_2$−COO-), 2.6 (J = 7.5 Hz, t, 2H, −$\underline{CH_2}$−COO−), 4.1 (J = 6.9 Hz, q, 2H, $CH_3$−$\underline{CH_2}$−O−), 7.1 (J = 6.3 Hz, d, 1H, Ar−H), 7.2 (J = 7.2 Hz, d, 2H, Ar−H), 7.3 (s, 1H, Ar−H), 8.0 (J = 9 Hz, d, 1H, Ar−H), 8.07 (J = 6.9 Hz, d, 2H, Ar−H). $^{13}$C-NMR (500 MHz, $CDCl_3$) $\delta$/ppm: 173.19 (COO), 171.77 (C=N), 159.11, 54.43, 149.28, 147.38, 136.38, 125.88, 125.37, 122.60, 116.98, 104.91 for aromatic carbons, 64.21 (−O−$CH_2$−$CH_3$), 34.45, 31.93, 29.69, 29.66, 29.61, 29.46, 29.36, 29.26, 29.10, 24.87, 22.70 for methylene carbons [$CH_3$−$(CH_2)_{12}$−COO−], 14.77 (−O−$CH_2$−$\underline{CH_3}$), 14.14 [$\underline{CH_3}$− $(CH_2)_{12}$−COO−].

## 3. Results and Discussion

### *3.1 Anisotropic Behavior and Liquid Crystallinity of nEBTHDZ*

The transition temperatures and associated enthalpy changes of ***n*EBTHDZ** obtained from the DSC measurements are summarized in Table 1 wherein all the title compounds exhibit enantiotropic mesophase [19]. Representative DSC thermograms for **15EBTHDZ** upon heating and cooling cycles are shown in Fig. 1. From Fig. 1, it shows the phase sequence of crystal-nematic-isotropic (Cr-N-I) and vice-versa upon heating and cooling processes.

**Table 1.** Phase sequences and associated enthalpy changes for ***n*EBTHDZ** upon heating and cooling

| Compound | Phase transition temperature, °C heating (associated enthalpy change, kJ $mol^{-1}$) cooling |
|---|---|
| **5EBTHDZ** | $Cr_1$ 85.9(3.3) $Cr_2$ 115.4(30.2) N 150.8(1.1) I I 149.1(1.1) N 87(31.2) Cr |
| **7EBTHDZ** | Cr 100.7(34) N 143.4(0.9) I I 141.9(0.8) N 74(30.8) Cr |
| **9EBTHDZ** | Cr 106.8(38.8) N 137.7(1.2) I I 136.2(0.9) N 76.1(38.8) Cr |
| **11EBTHDZ** | Cr 106.5(40) N 132.5(0.9) I I 131.3(0.9) N 77.9(40.7) Cr |
| **13EBTHDZ** | Cr 108.5(45) N 127.8(0.8) I I 126.6(0.7) N 78.3(47.7) Cr |
| **15EBTHDZ** | Cr 110.4(40.6) N 123(1.0) I I 122.3(1.1) N 88.2(45.5) Cr |
| **17EBTHDZ** | Cr 112.3(57.3) N 120(1.3) I I 119(1.5) N 92.7(68.3) Cr |

*Note*: Cr, crystal; N, nematic; I, isotropic.



The low enthalpy values for N-I on heating (1.0 kJ $mol^{-1}$) and cooling (1.1 kJ $mol^{-1}$) agree with the reversible transition of isotropization and crystallization.

Observation under crossed polarized light reveals that all the compounds are purely nematogens as those analogous compounds reported in the literature [20]. Upon cooling of **15EBTHDZ** from its isotropic liquid phase, for instance, the nematic droplets appeared (Fig. 2(a)) which coalesced to form the schlieren texture with typical twofold and fourfold brushes (Fig. 2(b)). In this series, the compound with shortest alkoxyl chain (**5EBTHDZ**) has shown an exceptional feature in which a crystal–crystal ($Cr_1$-$Cr_2$) transition is also observed before it melts from crystal to nematic phase at 115.4°C similar to the phenomenon reported in our earlier literature [21].

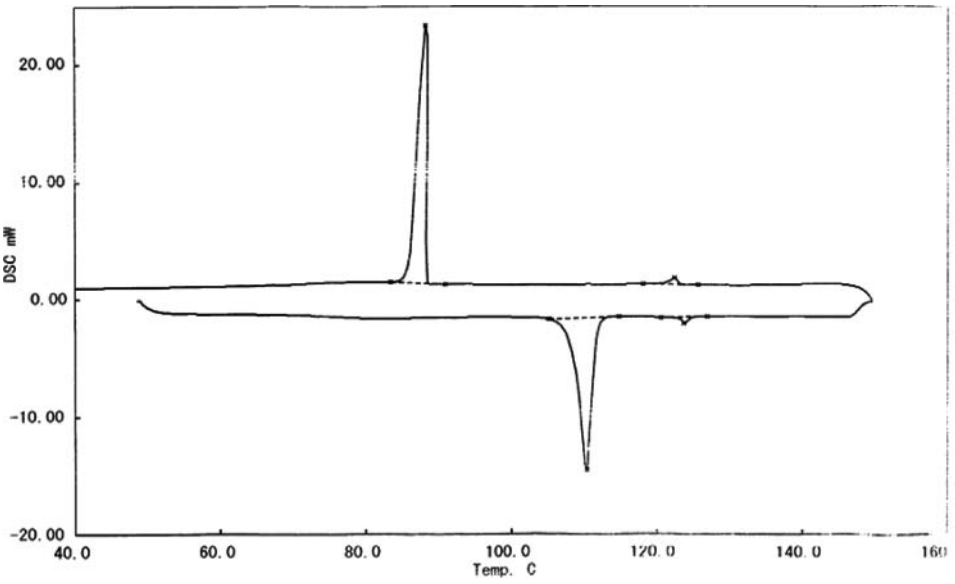



**Figure 1.** DSC thermogram of **15EBTHDZ** at heating and cooling rates of ±5°C $min^{-1}$.

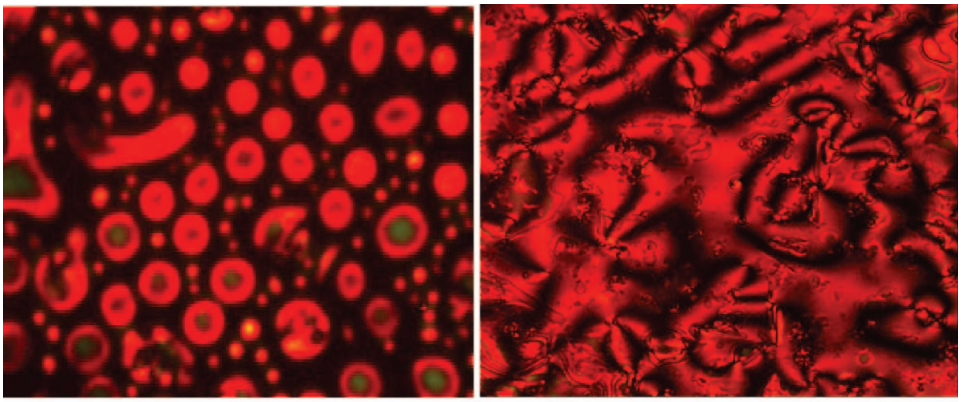



**Figure 2.** Optical photomicrograph of **15EBTHDZ** showing (a) the formation of nematic droplets, and (b) the schlieren texture with twofold and fourfold brushes upon cooling.

A plot showing the transition temperatures against the number of carbons in the alkoxyl carbon chain $OOCC_nH_{2n+1}$ of ***n*EBTHDZ** during the heating scan is shown in Fig. 3. The melting temperature ($T_{Cr-N}$) decreases when the number of carbon in the alkyl group $OOCC_nH_{2n+1}$ varied from $n = 5$ (115.4°C) to $n = 7$ (100.7°C). This can probably be rationalized by the fact that **5EBTHDZ**, which possesses a relatively low length-to-breadth ratio and higher rigidity among this series, favors a rigid rod conformation which helps to enhance the binding forces among the orderly positioned molecules within the crystal lattice [22].

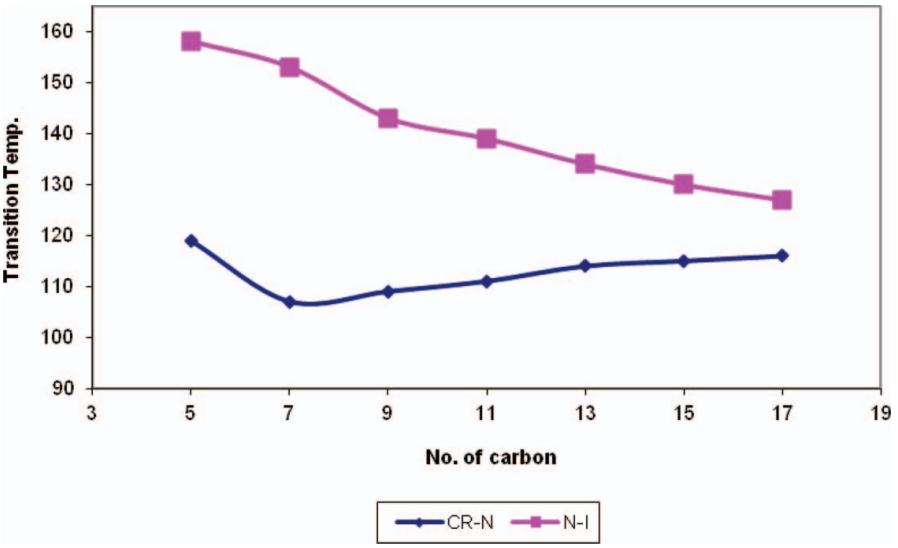



**Figure 3.** Plot of transition temperatures versus the number of carbons ($n$) in the alkoxyl chain of ***n*EBTHDZ** during heating cycle.

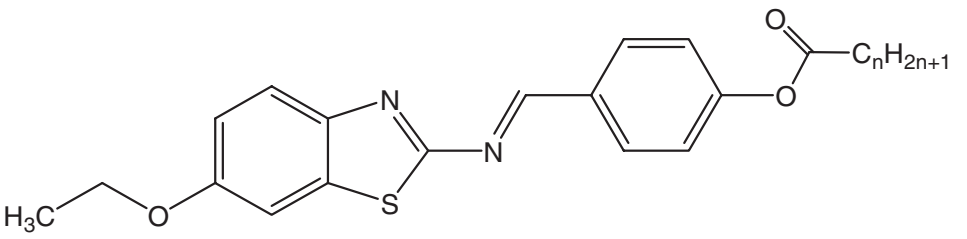
However, the melting temperatures showed a drastic rise from $n = 7$ to $n = 9$ before it become almost plateau from $n = 9$ to $n = 11$ and, subsequently, experienced a minor increase from $n = 11$ to $n = 17$. This phenomenon can be attributed to the increased intermolecular Van der Waals attraction when the length of the alkoxyl chain increased [23].

Figure 3 illustrates a linear descending trend in clearing temperatures ($T_{N–I}$) when title compound changes from **5EBTHDZ** to the member with higher *n*. This result can be ascribed to the dilution of mesogenic core, and this phenomenon has presumably resulted from the increase in the length of the terminal chain [24, 25]. Similar descending trend was also reflected on the homologous series of 6-ethoxy-2-(4-alkoxybenzylidenamino)benzothiazole in which the homolog with the longest terminal chain possesses the lowest thermal stability [26].



### *3.2 Comparison Studies Between Title Compounds With 6-ethoxy-2-(4-alkanoxybenzylidenamino)benzothiazole, nEBABTH*

In order to reveal the effect of the bridging group N=N on mesomorphic properties, the molecular structures and phase behaviors of the title compounds were compared with recently reported mesogenic compounds ***n*EBABTH** [20] in which ***n*EBABTH** comprised of a benzothiazole and phenyl esters linked by an imine C=N group. The general molecular structure of the reported ***n*EBABTH** is shown below:




A linear descending trend of melting temperatures was initially observed when it changed from **5EBABTH** to **9EBABTH.** However, the melting temperature increases when the alkoxyl chain is elongated from $n = 9$ until $n = 17$. In addition, the smectic phase, which was absent in the title compounds, was observed in even parity from **9EBABTH** to **17EBABTH**. The differing anisotropic properties between ***n*EBABTH** and the title compounds can be ascribed to the variation in dipole moment. It has well been accepted that the C=N group is more polar than the N=N moiety due to the presence of the effective charge between C and N while in the azo group the dipole moment is zero [27]. This has also been concurred by Gray that the dipole moment is an important factor as far as the relative thermal stability of smectic phase is concerned [23]. The greater dipole moment led to enhanced polarizability and increase in intermolecular cohesive forces. As such, it helps to widen the mesophase range and increase the thermal stability of smectic phase. Hence, the majority of the domains observed from **9EBABTH** to **17EBABTH** exhibited smectogenic as well as nematogenic properties when the temperatures increased.

The azo linkage (N=N) between the benzothiazole and phenyl ester in the present compounds ***n*EBTHDZ** confers stepped core structure leading to the broadening effect and, hence, disrupts the lamellar packing [26]. Therefore, only the nematic phase is dominant in ***n*EBTHDZ**.

## 4. Conclusions

All the target compounds exhibited enantiotropic nematic phase. The length of the terminal alkoxyl chain affects the melting and clearing temperatures. The azo linking group, which has intersected between the benzothiazole and an aromatic esters, is a dominating factor which limits the formation of nematic phase only in the target compounds. The study also revealed that the mesophase range was greatly affected by the length of the alkoxyl carbon chain of $OOCC_nH_{2n+1}$.

## Acknowledgment

The authors would like to thank Universiti Sains Malaysia for funding the project through FRGS Grant (Account No. 203/PKIMIA/6711192).



## References

[1] Matharu, A. S., & Chambers-Asman, D. (2007). *Liq. Cryst.*, *34*, 1317–1336.
[2] Gallardo, H., Magnago, R. F., & Bortoluzzi, A. J. (2001). *Liq. Cryst.*, *28*, 1343–1352.
[3] Seed. (2007). *A. Chem. Soc. Rev.*, *36*, 2046–2069.
[4] Lai, C. K., Ke, Y., Chien-Shen, J. S., & Li, W. (2002). *Liq. Cryst.*, *29*, 915–920.
[5] Lai, L. L., Wang, C. H., Hsien, W. P., & Lin, H. C. (1996). *Mol. Cryst. Liq. Cryst.*, *287*, 177–181.
[6] Petrov, V. F., Pavluchenko, A. I., & Smirnova, N. I. (1995). *Mol. Cryst. Liq. Cryst.*, *265*, 47–53.
[7] Parra, M., Belmar, J., Zunza, H., Zuniga, C., Villouta, S., & Martinez, R. Bol. (1993). *Soc. Chil. Quim.*, *38*, 325–330.
[8] Campbell, N. L., Duffy, W. L., Thomas, G. I., Wild, J. H., Kelly, S. M., Bartle, K., O'Neill, M., Minter, V., & Tuffin, R. P. (2002). *J. Mater. Chem.*, *12*, 2706–2721.
[9] Ha, S. T., Koh, T. M., Lin, H. C., Yeap, G. Y., Win, Y. F., Ong, S. T., Sivasothy, Y., & Ong, L. K. (2009). *Liq. Cryst.*, *36*, 917–925.
[10] Ha, S. T., Koh, T. M., Ong, S. T., & Ong, L. K. (2009). *Molbank, M.*, *606*, 1–3.
[11] Yoshino, K., Tanaka, N., & Inuishi, Y. (1976). *Jpn. J. Appl. Phys.*, *15*, 735.
[12] Kusabayashi, S., & Labes, M. M. (1969). *Mol. Cryst. Liq. Cryst.*, *7*, 395.
[13] Funahashi, M., & Hanna, J. I. (1996). *Jpn J. Appl. Phys.*, *35*, L703–L705.
[14] Funahashi, M., & Hanna, J. I. (1997). *Phys. Rev. Lett.*, *78*, 2184–2187.
[15] Funahashi, M., & Hanna, J. I. (1997). *Mol. Cryst. Liq. Cryst.*, *304*, 429–434.
[16] Prajapati, A. K., & Bonde, N. L. (2006). *J. Chem. Sci.*, *118*(2), 203.
[17] Demus, D., & Richter, L. (1978). *Textures of Liquid Crystals*, Verlag Chemie: New York.
[18] Dierking, I. (2003). *Textures of Liquid Crystals*, Wiley-VCH: Weinheim.
[19] Kumar, S. (2001). *Liquid Crystals Experimental Study of Physical Properties and Phase Transitions*, Cambridge University Press: Cambridge.
[20] Ha, S. T., Koh, T. M., Yeap, G. Y., Lind, H. C., Leee, S. L., Wina, Y. F., & Ong, S. T. (2010). *Phase Transitions*, *83*, 195–204.
[21] Yeap, G. Y., Ha, S. T., Lim, P. L., Boey, P. L., Mahmood, W. A. K., Ito, M. M., & Sanehisa, S. (2004). *Mol. Cryst. Liq. Cryst.*, *423*, 73–84.
[22] Collings, P. J., & Hird, M. (1998). *Introduction to Liquid Crystals: Chemistry and Physics*, Taylor & Francis: London.
[23] Gray, G. W. (1962). *Molecular Structure and Properties of Liquid Crystals*, Academic Press: London.
[24] Yeap, G. Y., Ha, S. T., Lim, P. L., Boey, P. L., Ito, M. M., Sanehisa, S., & Youhei, Y. (2006). *Liq. Cryst.*, *33*, 205.
[25] Yeap, G. Y., Hng, T. C., Mahmood, W. A. K., & Adnan, R. (2006). *Mol. Cryst. Liq. Cryst.*, *452*, 49–61.
[26] Vieira, A. A., Cristiano, R., Bortoluzzi, A. J., & Gallardo, H. (2007). *J. Mol. Struct.*, *875*, 364.
[27] Carey, A. F. (2003). *Organic Chemistry*, 5th Ed., McGraw Hill: New York.